



Quinone-formaldehyde polymer as an active material in Li-ion batteries



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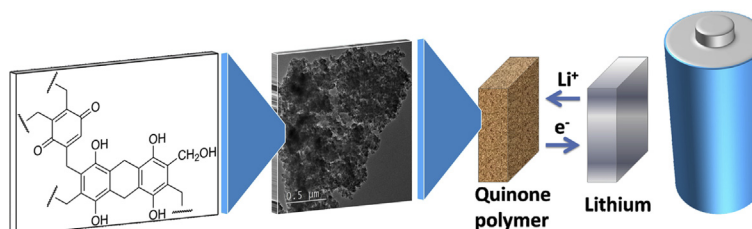
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HIGHLIGHTS

- Quinone-formaldehyde polymer (BQP) synthesis and characterization.
- Problematic purification, characterization due to non-solubility.
- Testing of BQP in different electrolytes (best LiTFSI/DOL + DME).
- Achieving supreme cycling stability compared to other benzoquinones.
- Optimization of BQP synthesis is needed to get closer to the theoretical capacity.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 23 September 2015

Received in revised form

28 December 2015

Accepted 3 March 2016

Keywords:

Lithium batteries

Organic electrodes

Electroactive polymers

Quinones

ABSTRACT

A benzoquinone polymer is synthesized by the polymerisation of hydrobenzoquinone and formaldehyde, followed by oxidation process using a hydrogen peroxide to convert hydroquinone to quinone. As prepared materials are characterized with FTIR, ¹H-¹³C CPMAS NMR, pyrolysis coupled with gas chromatography (GC) and mass spectrometer (MS), TGA-MS analysis, EDX, elemental analysis, XRD, SEM and TEM microscopies and BET nitrogen adsorption. The benzoquinone polymer shows an excellent electrochemical performance when used as a positive electrode material in Li-ion secondary batteries. Using an electrolyte consisting 1 M bis(trifluoromethane)-sulfonimide lithium salt dissolved in 1,3-dioxolane and dimethoxyethane in a vol. ratio 1:1 (1 M LiTFSI/DOL + DME = 1:1) a stable capacity close to 150 mAh/g can be obtained. Compared to other electroactive materials based on benzoquinones it has a supreme capacity stability and is prepared by a simple synthesis using easily accessible starting materials. Further improvements in the capacity value (up to the theoretical value of 406 mAh/g) can be foreseen by achieving a higher degree of oxidation and by modification of polymerization process to enhance the electronic and ionic conductivity.

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1. Introduction

Current economy strongly relies on non-sustainable and limited energy resources based on fossil fuels and nuclear energy. Additionally, the use of non-renewable resources raises environmental

problems such as CO₂ emission, nuclear waste, or release of PM10 particles. Renewable energy resources like solar or wind energy have a potential to replace the non-renewables, however prior that the issues related to their intermittent nature need to be appropriately solved. Transformation of electrical energy into mechanical and back to electrical is already very well established but not feasible at all locations. Novel generations of batteries using sustainable chemistries can play an important role in overcoming

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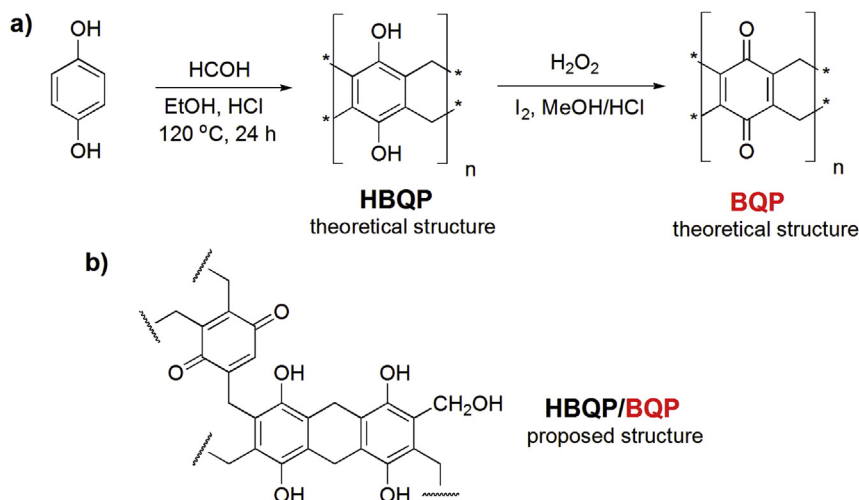


Fig. 1. a) Reaction scheme and b) Proposed structure of HBQP/BQP sample.

these difficulties. While currently most of the efforts are devoted to the development of Li-S and metal-air batteries, organic redox active materials are not very well explored. Tarascon et al. [1] showed that very high specific capacities (up to 600 mAh/g) can be obtained from the abundant resources, but unfortunately during cycling their capacity tends to fade rapidly. The main reasons for capacity degradation are the dissolution of organic materials in organic solvents, irreversible reactions by radical anions and the low inherent conductivity of these materials [2–4]. At least partly, solubility can be suppressed by polymerization [5–10], entrapment of organic molecules inside highly porous materials [11,12], grafting on insoluble carriers [2,13,14] or using ion-selective separators (ceramic, gel, polymer, etc.) [4,15–17]. Another possibility is to use dissolved active organic compounds in the redox flow type of batteries [18–20].

Benzoquinone is one of the most promising organic active materials to be used in secondary Li-batteries. Due to the small molecular mass and ability to exchange two electrons, its theoretical capacity is as high as 496 mAh/g. Its discharge potential is about 2.8 V versus metallic lithium [12], which is considerably higher than in most other carbonyl organic compounds with typical potentials in the range of 1.8–2.6 V [5]. The significant capacity degradation of benzoquinone is connected to the formation of highly reactive radical anions during electrochemical reduction and their irreversible reactions with electrolyte [3,4,8,15,21]. More bulky anthraquinones with sterically protected radical anions usually exhibit much better reversibility. Due to their higher molecular mass, anthraquinones are limited to theoretical capacities of 260 mAh/g and possess lower redox potential at around 2.2 V vs. lithium which makes them less attractive for high energy density materials despite some good results in Li-batteries [7,11,22–28]. By appropriate substitution of benzoquinone ring radical anions can be stabilized leading to reversible redox reactions (similar to anthraquinone). Some examples of substituted benzoquinones are: 2,5-dimethoxy-*p*-benzoquinone [3], 2,5-diethoxy-*p*-benzoquinone [15], 2,5-dihydroxy-*p*-benzoquinone [29], calix [4]-*p*-benzoquinone [30], tetramethoxy-*p*-benzoquinone [31] and others. Despite the important improvements towards achievement of better reversibility of redox reactions, the problem of quinone solubility in organic electrolytes used in Li-ion batteries has not been solved satisfactorily and capacity fading remains one of the central issues. In addition, the use of substituents increases the molecular mass of active material which decreases its specific capacity. Another

strategy is using lithium salts of active materials which lowers their solubility in organic solvents and improves cyclability. Examples are: dilithium salt of 3,6-dihydroxy-2,5-dimethoxy-*p*-benzoquinone [32], dilithium salt of 2,5-dihydroxy-*p*-benzoquinone [33], tetralithium salt of tetrahydroxy-*p*-benzoquinone [34], tetralithium salt of 2,5-dihydroxyterephthalic acid [35], dilithium rhodizonate [1] and dilithium chloranilate [36]. At the same time the negative charge on active materials lowers the redox potential which is less desirable. Most likely, the optimal approach is a cross polymerization of quinones, which keeps the values of capacity and redox potential close to those of benzoquinone. The resulting polymers are typically insoluble in the electrolytes which enables stable capacities [37–39].

In this work we show a simple approach to the synthesis of a highly porous and crosslinked benzoquinone formaldehyde resin (BQP), which enables good wettability (ionic wiring) and insolubility of the resulting polymer in the electrolytes. The main approach which starts with the synthesis of hydrobenzoquinone polymer (HBQP) has been adopted from the literature and is schematically shown in Fig. 1a [40]. HBQP is then oxidized with H₂O₂ using iodine as a catalyst to obtain a benzoquinone polymer (BQP) (Fig. 1a) [41]. The obtained sample was characterised using a range of different solid state characterisation techniques. A complex structure of HBQP and BQP can be proposed, with a variable ratio of hydroquinone/quinone rings and with incomplete cross-linking as indicated in Fig. 1b. In contrast to HBQP, the oxidized counterpart (BQP) shows a higher electrochemical activity and a stable electrochemical behaviour when used as a positive electrode material in Li-organic batteries.

2. Experimental

Compound HBQP: Hydroquinone-formaldehyde polymer was synthesized according to the following procedure [40]: hydroquinone (8.80 g, 80 mmol) and 37 wt. % formaldehyde (16.0 mL, 215 mmol) were dissolved in a mixture of 30 mL of ethanol and 2.8 mL of concentrated hydrochloric acid in a 150 mL autoclave with a Teflon lining. The autoclave was then sealed and heated in an oven at 120 °C for 24 h. The resulting black gel was ground and soaked in 50 g of stirred ethanol for 12 h. Finally, the slurry was filtrated and washed with ethanol. The filter cake was air-dried to a state that had an ethanol content of about 80 wt. %. Then, the friable filter cake was ground into powder and further dried at 120 °C in a

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